

PATENT SPECIFICATION

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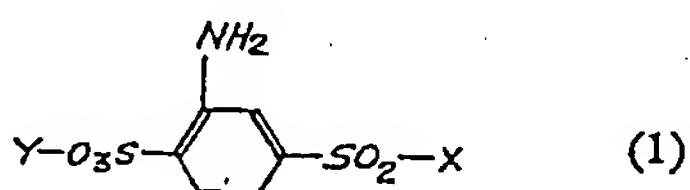
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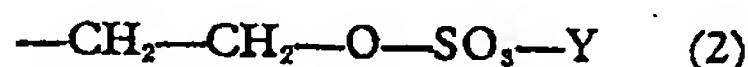


(54) PROCESS FOR THE PRODUCTION OF 1-AMINOBENZENE-5-β-SULPHATOETHYLSULPHONE- 2-SULPHONIC ACID AND 1-AMINOBENZENE-5- VINYLSULPHONE-2-SULPHONIC ACID AND THE ALKALI METAL AND ALKALINE EARTH METAL SALTS THEREOF

(71) We, HOECHST AKTIEN-
 GESELLSCHAFT, a body corporate
 organised according to the laws of the
 Federal Republic of Germany, of 6230 Frank-
 furt/Main 80, Postfach 80 03 20, Federal
 Republic of Germany, do hereby declare the
 invention for which we pray that a patent may
 be granted to us, and the method by which
 it is to be performed, to be particularly des-
 cribed in and by the following statement:—
 The present invention provides a process
 for the production of compounds of the general
 formula (1)



wherein X represents a group of the formula

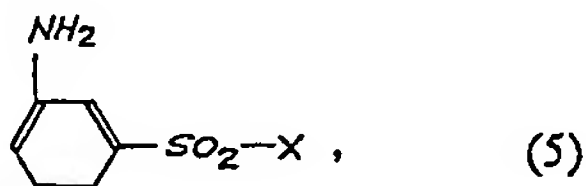


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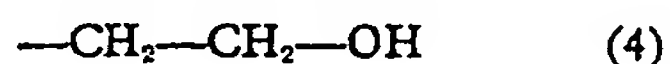


and Y represents hydrogen, an alkali metal or
 alkaline earth metal salt thereof. The prepared
 alkali metal and alkaline earth metal com-
 pounds are the sodium, potassium and cal-
 cium/salts.

The novel process comprises sulphonating
 a compound of the formula (5)



in which X has the above meaning or repre-
 sents a radical of the formula (4)



wherein a compound of the formula (5) is
 dissolved or suspended in a mixture of sul-
 phuric acid and sulphur trioxide containing
 up to 30% by weight of sulphur trioxide, or
 in a mixture of sulphuric acid and chlorosul-
 phonic acid, at between -15°C and $+40^\circ\text{C}$,
 preferably between $+10$ and 20°C , whereby
 there is used for the sulphonation a total of
 from two to two and a half times the
 stoichiometrical amount of active sulphur tri-
 oxide or from one to one and a half times the
 stoichiometrical amount of chlorosulphonic
 acid calculated on the amount of the com-
 pound of the formula (5) having a radical of
 the formula (2) or (3), or when starting from
 a compound of the formula (5) having the
 radical of the formula (4) for conversion *in*
situ into a compound of the formula (1) hav-
 ing a radical of the formula (2), using in total
 three to three and a half times the stoichio-
 metrical amount of active SO_3 or from two to
 two and a half times the stoichiometrical
 amount of chlorosulphonic acid, and subse-
 quently heating the reaction mixture to 155 —
 165°C , preferably to 158 — 162°C , and con-
 tinuing the reaction at this temperature for
 some time, for example 1 to 6 hours.

The compound of formula (5) may be dis-
 solved or suspended in such a way that it is
 dissolved or suspended either immediately in
 the oleum required having up to 30% by
 weight of SO_3 and the required stoichio-
 metrical amount of SO_3 mentioned above or
 in the mixture of sulphuric acid and chloro-
 sulphonic acid having the necessary stoichio-
 metrical amount of chlorosulphonic acid men-
 tioned above, or it may be first dissolved or
 suspended in 100% sulphuric acid or in oleum
 containing up to 30% by weight of SO_3 or in
 a mixture of sulphuric acid and chlorosul-
 phonic acid, using in each case a smaller
 amount than the above-mentioned stoichio-
 metrically required amount of SO_3 or chloro-
 sulphonic acid, and then adding oleum or

2 sulphur trioxide or chlorosulphonic acid in such an amount that the sulphonation mixture contains in total the required two to two and a half times the stoichiometrical amount of
5 active sulphur trioxide or from one to one and a half times the stoichiometrical amount of chlorosulphonic acid.

10 A quantitative isolation of the free sulphonic acids of formula (1) is not possible because of their very good solubility. Since their use on an industrial scale preferably takes place in the form of salts, the sulphonation mixture is poured onto ice and the sulphuric acid in excess is neutralised with an
15 alkali metal or alkaline earth metal hydroxide or carbonate in order to isolate the sulphonic acids salts of formula (1). After filtering the precipitate of alkali metal or alkaline earth metal sulphate, the sulphonic acids may be obtained by spray-drying in the form
20 of the alkali metal or alkaline earth metal salts, preferably the sodium or potassium salt.

25 The yield of the sulphonic acids of general formula (1) is 75 to 95% of the theory, calculated on the free acid.

In comparison with the state of the art it could not have been foreseen that the 1 - aminobenzene - 5 - sulphone - 2 - sulphonic acids of the general formula (1) could be obtained by using double to two and a half
30 times the stoichiometrical amount of active sulphur trioxide or from one to one and a half times the stoichiometrical amount of chlorosulphonic acid at about 160°C, for according to the sulphonation process of German Offenlegungsschrift No. 2,352,059 starting from a compound of the formula (5) the
35 1 - aminobenzene - 5 - β - sulphatoethylsulphone - 2,4 - disulphonic acid is formed by reaction with the threefold stoichiometrical amount of active sulphur trioxide at 125—135°C. A reduction of the amount of active sulphur trioxide in this process leads only to a reduced yield of disulphonation product
40 together with larger amounts of the starting product.

45 It was therefore unexpected that an increase of temperature of 30 to 35°C would lead to monosulphonation; it was rather to be expected that a shifting of the ratio of preliminary product and disulphonation product in the mixture would take place.
50

55 The structure of the 1 - aminobenzene - 5 - vinylsulphone - 2 - sulphonic acid obtained was ascertained by chromatographic and infra-red spectroscopic identification. The substance for comparison was prepared by starting from 1 - chloro - 2 - nitrobenzene - 4 - sulphochloride which was reduced to 1 -
60 chloro - 2 - nitrobenzene - 4 - sulphonic acid, reacting the latter with ethylene oxide to form 1 - chloro - 2 - nitrobenzene - 4 - β - hydroxyethylsulphone and then exchanging the chlorine atom for the sulphonic acid radical
65 by reacting with sodium or potassium sul-

phite, reducing the nitro group to the amino group, esterifying the hydroxy group and converting the ester into the vinyl derivative.

However, this process for preparing 1 - aminobenzene - 5 - vinylsulphone - 2 - sulphonic acid carried out in the laboratory
70 would cause problems on an industrial scale since the intermediate products 1 - chloro - 2 - nitrobenzene - 4 - sulphochloride and 1 - chloro - 2 - nitrobenzene - 4 - β - hydroxyethyl sulphone made during the preparation
75 cause injury to the skin and produce allergies, so that a large expenditure of technical equipment would be necessary to prepare these compounds industrially without any risk. 80

The 1 - aminobenzene - 5 - β - sulphatoethylsulphone - 2 - sulphonic acid and 1 - aminobenzene - 5 - vinylsulphone - 2 - sulphonic acid are used as diazo components in the preparation of valuable azo dyestuffs, as described for example in German Offenlegungsschriften Nos. 2,161,760 and 2,222,032. Such azo dyestuffs are reactive
85 dyestuffs for the fast dyeing of natural and synthetic cellulose fibres for example cotton and spun rayon or nitrogen-containing fibres for example wool and polyamide fibres. 90

The following Examples illustrate the invention. Parts and percentages are by weight unless otherwise stated. 95

EXAMPLE 1

28 Parts of 1 - aminobenzene - 3 β - sulphatoethyl - sulphone were introduced portionwise while cooling and stirring and exclusion of air humidity, into 100 parts of sulphuric acid monohydrate at 15—20°C. Stirring was continued for three hours, and then 25 parts of oleum having a content of SO₃ of 65 percent by weight were slowly added dropwise, and the temperature maintained at 15—20°C by external cooling. The whole was heated for 6 hours at 158—160°C. The cooled reaction mixture was then poured onto ice while stirring. 100

110 The 1 - aminobenzene - 5 - β - sulphatoethylsulphone - 2 - sulphonic acid thus obtained could be further processed directly in solution without intermediate isolation, for example by diazotisation.

115 After neutralizing the solution by addition of acid binding agents, for example alkali metal or alkaline earth metal carbonates or alkali hydroxides, difficultly soluble sulphates for example calcium sulphate, being separated if necessary, the 1 - aminobenzene - 5 - β - sulphato - ethylsulphone - 2 - sulphonic acid could be isolated by evaporation as alkali metal or alkaline earth metal salt. The yield was 80% of theory. 120

EXAMPLE 2

125 20 Parts of 1 - aminobenzene - 3 - β - hydroxyethyl sulphone were introduced portionwise while cooling and stirring and ex-

clusion of air humidity, into 100 parts of sulphuric acid monohydrate at 15—20°C. Stirring was continued for 3 hours, and then 25 parts of liquid sulphur trioxide were slowly added dropwise, the temperature being maintained at 15—20°C by external cooling. The mixture was subsequently heated for 6 hours at 158—160°C.

The cooled mixture was then poured onto ice. The mixture was worked up as indicated in Example 1. The yield of 1 - aminobenzene - 5 - β - sulphatoethylsulphone - 2 - sulphonic acid was 85% of theory.

The 1 - aminobenzene - 5 - β - sulphatoethylsulphone - 2 - sulphonic acid or the alkali metal or alkaline earth metal salts thereof could be converted by heating for one hour in 200 parts of an aqueous dilute sodium hydroxide solution at a pH value of 11 into the alkali metal or alkaline earth metal salts of 1 - aminobenzene - 5 - β - hydroxyethylsulphone - 2 - sulphonic acid which could be isolated after neutralization of the alkaline reaction solution with hydrochloric acid by spray-drying.

EXAMPLE 3

18 Parts of 1 - aminobenzene - 3 - vinylsulphone were introduced portionwise while cooling and stirring and exclusion of air humidity into 100 parts of sulphuric acid monohydrate at 15—20°C. Stirring was continued for three hours, and then 25 parts of oleum having a content of SO₃ of 65% by weight were slowly added dropwise, the temperature being maintained at 15—20°C by external cooling. The mixture was then heated for 6 hours at 158—160°C. The cooled reaction mixture was added to ice while stirring. Working up was carried out as indicated in Example 1. The yield of 1 - aminobenzene - 5 - vinylsulphone - 2 - sulphonic acid was 80% of theory.

EXAMPLE 4

28 Parts of 1 - aminobenzene - 3 - β - sulphatoethylsulphone were introduced portionwise at 15—20°C while cooling and stirring and exclusion of air humidity, into 90 parts of sulphuric acid monohydrate. Stirring was continued for three hours, and 13 parts of chlorosulphonic acid were slowly added dropwise, the temperature being maintained at 15—20°C by external cooling. Subsequently, the mixture was heated for three hours at 160°C. The cooled reaction mixture was then poured onto ice and the mixture worked up as indicated in Example 1.

The yield of 1 - aminobenzene - 5 - β - sulphatoethylsulphone - 2 - sulphonic acid was 85% of theory.

EXAMPLE 5

20 Parts of 1 - aminobenzene - 3 - β - hydroxyethylsulphone were introduced portion-

wise at 15—20°C while cooling and stirring and exclusion of air humidity, into 90 parts of sulphuric acid monohydrate. Stirring was continued for three hours, and then 25 parts of chlorosulphonic acid were slowly added dropwise, the temperature being maintained at 15—20°C by external cooling. The mixture was then heated for 3 hours at 160°C. The cooled reaction mixture was added to ice while stirring. The mixture was worked up as indicated in Example 1. The yield of 1 - aminobenzene - 5 - β - sulphatoethylsulphone - 2 - sulphonic acid was 85% of theory.

EXAMPLE 6

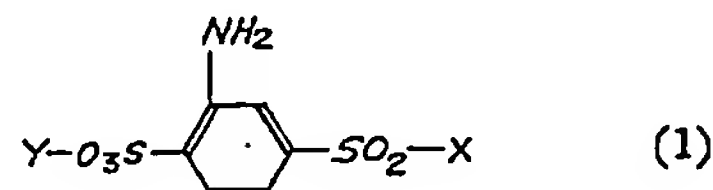
18 Parts of 1 - aminobenzene - 3 - vinylsulphone were introduced portionwise at 15—20°C while cooling and stirring and exclusion of air humidity, into 90 parts of sulphuric acid monohydrate. Stirring was continued for three hours at this temperature and then 13 parts of chlorosulphonic acid were slowly added dropwise, the temperature being maintained at 15—20°C by external cooling. The mixture was heated for three hours at 160°C. The cooled reaction mixture was then added to ice while stirring. The mixture was worked up as indicated in Example 1. The yield of 2 - aminobenzene - 5 - vinylsulphone - 2 - sulphonic acid was 80% of theory.

EXAMPLE 7

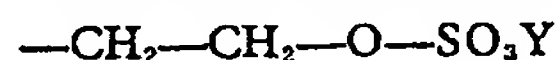
20 Parts of 1 - aminobenzene - 3 - β - hydroxyethylsulphone were introduced portionwise at 15—20°C while cooling and stirring and exclusion of air humidity, into 125 parts of oleum having a content of SO₃ of 20% by weight. Stirring was continued for three hours at this temperature, and the mixture was then heated for 6 hours at 158—160°C. The cooled reaction mixture was then added to ice. The mixture was worked up as indicated in Example 1. The yield of 1 - aminobenzene - 5 - β - sulphatoethylsulphone - 2 - sulphonic acid was 85% of theory.

WHAT WE CLAIM IS:—

1. A process for the production of a compound of the general formula (1)



wherein X represents a group of the formula

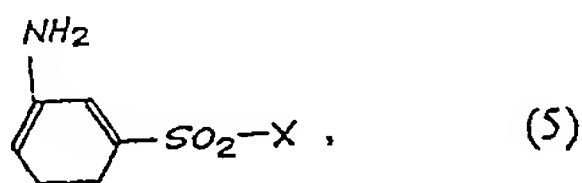


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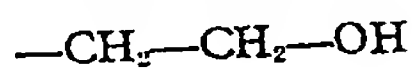


and Y represents hydrogen, an alkali metal or alkaline earth metal equivalent, which comprises dissolving or suspending at a tempera-

ture of -15°C to $+40^{\circ}\text{C}$, a compound of the general formula (5)



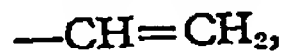
5 which X has the above meaning or X represents a radical of the formula



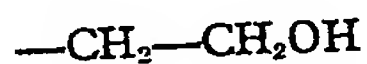
10 in a mixture of sulphuric acid and sulphur trioxide containing up to 30% by weight of sulphur trioxide, or in a mixture of sulphuric acid and chlorosulphonic acid using in total two to two and a half times the stoichiometrical amount of active sulphur trioxide or from one to one and a half times the stoichiometrical amount of chlorosulphonic acid when starting from a compound of the formula (5) having a radical of the formula



or



20 or when starting from a compound of the formula (5) having the radical of the formula



25 using in total three to three and a half times the stoichiometrical amount of active sulphur trioxide or from two to two and a half times

the stoichiometrical amount of chlorosulphonic acid, calculated in each case on the amount of the compound of the formula (5), and subsequently heating the reaction mixture to $155\text{--}165^{\circ}\text{C}$ and continuing the reaction at this temperature for sometime and, if desired, converting the free sulphonic acid obtained of the formula (1) into the alkalimetal or alkaline earth metal salt by neutralization with an alkali metal or alkaline earth metal hydroxide or carbonate and isolating said salt.

2. A process as claimed in claim 1 wherein the reaction mixture is heated to $158\text{--}162^{\circ}\text{C}$.

3. A process as claimed in claim 1 or 2 wherein the reaction mixture is heated from 1 to 6 hours.

4. A process as claimed in claim 1 conducted substantially as described herein or in any one of the Examples.

5. The compounds which have been prepared as claimed in any one of claims 1 to 4.

6. Any one of the compounds of formula (1) given in claim 1 which have been obtained as described in the Examples herein.

7. A process wherein a compound produced according to claim 1 is used for the synthesis of azo dyestuffs.

8. Azo dystuffs which have been prepared with any one of the compounds produced as described in claims 1 to 4.

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